A SIMPLIFIED REACTION MECHANISM FOR PROPANE COMBUSTION

J. M. Deur
Sverdrup Technology, Inc.
Lewis Research Center Group
Brook Park, Ohio

K. P. Kundu
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

Keywords: Reduced Mechanisms, Propane Combustion, Nitrogen Oxides

Abstract

A simplified reaction mechanism for propane combustion has been derived. This scheme is based on two competitive fuel decomposition reactions. Further, the combustion of hydrogen has been used to derive the concentrations of the intermediate reactive species, and the kinetic parameters for the rate equations are estimated through comparison of the species concentrations calculated using detailed mechanisms available in the literature. Calculated concentrations of nitrogen oxides (NO_x) and carbon monoxide found using this mechanism agree well with previously published experimental data.

Introduction

The principal pollutants released in hydrocarbon combustion are carbon monoxide, oxides of nitrogen, organic compounds (unburned and partially burned), and particulates, e.g., soot. In general, the observed concentrations of these various pollutant species differ from calculated equilibrium level concentrations, indicating the importance of reaction kinetics in determining pollutant emissions.

The formation and decomposition of some pollutants (carbon monoxide, organic compounds, soot, etc.) are important aspects of the overall combustion process. To understand the chemistry of these pollutant species, some knowledge of the hydrocarbon fuel combustion process is required. However, other pollutants, e.g., nitrogen oxides, form independently of the combustion process itself. Under these circumstances, it becomes possible to decouple the description of their formation from the combustion process. Even so, the reactions involving these pollutants are controlled by the environment established by the combustion process, and hence, their chemistry is still intimately connected to combustion.

Over the last decade, numerical combustion modeling has become an essential part of many research and development programs. Although combustion involves a complex coupling of chemistry and transport processes, early combustion modeling efforts treated the former in a very simplistic fashion. Unless the characteristic times for the flow field and the chemistry are widely disparate, the details of the flow field and the finite rate chemistry must be simultaneously taken into account. However, the computational burden soon becomes excessive since the level of complexity involved in such coupled calculations increases proportionately with the number of reacting species. One way to improve tractability is to reduce the number of reactions considered in a coupled solution with the flow field.

Hydrocarbon combustion is a very complex process, and any attempt to obtain a simplified reaction scheme can easily become a daunting task. During combustion, a fuel molecule breaks down into many different hydrocarbon fragments. Any reaction mechanism which aims to consider all of these fragments tends to become very large. While there have been attempts to simplify the detailed kinetic mechanisms by algebraic (1,2,3) and other techniques (4,5), it is difficult to say if any such simplified scheme can substitute the detailed mechanisms, and while a few global reaction mechanisms (6,7,8,10) have been reported, their utility in practical applications where the levels of pollutants must be calculated has not been established.

The level of detail required to obtain the concentrations of species, particularly minor constituents such as the oxides of nitrogen, is difficult to determine. Although a detailed kinetic mechanism is sometimes required to understand the process, a global reaction scheme involving a few reaction species will often suffice.

Of course, it must be emphasized that all descriptions of chemical kinetics are in real sense only approxima-

tions. Even detailed kinetic mechanisms are constructed on the basis of reproducing observable phenomena which are not necessarily singular events. Moreover, evaluation of specific rate constants over ranges of temperatures and pressures adequate for combustion modeling is a difficult problem. Thus, it cannot be assumed that any validated mechanism can be divided and the parts used to describe independent phenomena, unless the detailed mechanism was constructed in that way.

The objective here is to develop a semi-global reaction mechanism that can predict overall temperatures and concentrations of pollutants such as NO_x and CO.

A Simplified Reaction Mechanism

The formation of thermal NO_x is generally slow when compared to combustion itself(9). Therefore, the NO_x formation mechanism can be divided into two stages: initiation and NO_x formation.

In the initiation phase, the hydrocarbon molecule (propane in the current discussion) is broken down into hydrocarbon fragments (10), followed by hydrogen combustion reactions to generate the free radicals. For simplicity, only one type of hydrocarbon fragment, i.e., CH_2, will be tracked in the present mechanism.

The key steps in these reactions are:

$$C_3H_8 \rightarrow 3CH_2 + 2H$$

$$H + O_2 \rightleftharpoons O + OH$$

$$C_3H_8 + O \rightarrow 3CH_2 + H_2O$$

$$CH_2 + O \rightleftharpoons CO + H_2$$

$$H_2 + O \rightleftharpoons H + OH$$

These steps generate two key radical species, CO and H_2. Further reactions of these species lead to the formation of CO_2 and H_2O, the most important reaction for the disappearance of CO being:

$$CO + OH \rightleftharpoons CO_2 + H$$

In the second stage, the NO_x is formed. The two principal sources of nitrogen oxide are: (1) oxidation of atmospheric nitrogen at high temperatures (thermal NO_x), and (2) reactions between hydrocarbon fragments and atmospheric nitrogen (prompt NO_x).

The principal reactions for thermal NO_x involve two radical species, O and OH, which are formed during the initiation stage and are near equilibrium with the corresponding molecular species.

$$N_2 + O \rightleftharpoons N + NO$$

$$N + OH \rightleftharpoons NO + H$$

$$N + O_2 \rightleftharpoons NO + O$$

The above reactions do not correctly explain the effect of residence times on NO_x formation. To overcome this problem, the following semi-global reaction has been incorporated into the present mechanism:

$$N_2 + O_2 \rightarrow 2NO$$

which follows from the series of reactions:

$$N + O_2 \rightarrow NO + O$$

$$O + O \rightarrow O_2$$

$$N + N \rightarrow N_2$$

Thus, the present mechanism postulates the following reactions for thermal NO_x formation:

$$N + O_2 \rightleftharpoons N + NO$$

$$N + OH \rightleftharpoons NO + H$$

$$N_2 + O_2 \rightarrow 2NO$$

In fuel-rich flames, the rapid formation of NO near the flame zone cannot be explained by the equilibrium concentrations of O and OH. Although there is uncertainty in the mechanisms for such prompt NO_x formation, it is normally hypothesized that the principal product of initial reaction is HCN. In the present mechanism, it will be assumed that HCN is formed through the reaction between the hydrocarbon fragment CH_2 and N_2:

$$CH_2 + N_2 \rightleftharpoons HCN + NH$$

The product species, HCN and NH, are subsequently transformed into other species by other reactions in the fuel rich combustion environment. In the current mechanism, these steps have not been considered. Instead, we have assumed that HCN and NH are the representative nitrogenous species themselves.

Combining the above description of the thermal and prompt NO_x formation with the previous characterization of the hydrocarbon combustion, the reduced mechanism summarized in Table I results.

Reaction Rates

Most reaction rates are taken from the literature with minor adjustments to match ignition delay times, flame temperatures, and concentrations of species formed during reactions. The activation energy for the fuel fragmentation reaction is taken to be equivalent to the activation energy reported by Lefebvre (11) in an ignition delay measurement.

Validation of Mechanism

The purpose of this mechanism is to compute NO_x emissions, which as noted earlier, depend on temperature and concentrations of radicals. To examine the fidelity of the mechanism, studies based on well stirred reactor calculations have been performed using the LSENS program (12), with sensitivity analyses generated via the decoupled direct method of Radhakrishnan (13). Flame temperatures (Fig. 1) and species concentrations (Figs. 2 through 5) for various test conditions have been compared with results found with a standard detailed mechanism of Miller and Bowman (14).

However, since agreement between experimental data and computed results using the Miller and Bowman mechanism is less than satisfactory in the case of NO_x formation, direct comparisons between calculations based on the present mechanism and experimental data obtained by Anderson (15) have been made (Figs. 6 and 7). These experiments were conducted at an initial pressure of 5.5 atmospheres and initial temperatures of 600 K and 800 K, although comparisons are only shown at 800 K in the above figures.

Finally, since the ultimate use of the reduced mechanism is multi-dimensional reacting flow field calculations, the Anderson burner geometry has been modeled using KIVA-II (16) with the current mechanism. Favorable comparisons (Fig. 8) have been obtained with regards to the NO_x emission levels over the range of equivalence

ratios and residence times reported by Anderson.

References

1. Peters, N., and Kee, R. J., *Comb. and Flame*, Vol. 68, 1987, p. 7.

2. Paczko, G., et. al., *21st Sym. (Intl.) Comb.*, 1988, p. 739.

3. Chen, J. Y., and Dibble, R. W., *SAND-90-8447*, 1990.

4. Lam, S. H., *Recent Advances in Aerospace Sciences (C. Casci, Ed.)*, Academic Press, 1985.

5. Lam, S. H., and Goussis, D. A., *MAE Report No. 1799*, Princeton U., 1988.

6. Ying, S. J., and Nguyen, H. L., *AIAA Paper No. 90-0546*, 1990.

7. Westbrook, C.K., and Dryer, F. L., *Comb. Sci. Tech.*, Vol. 27 (1-2), 1989, p. 31.

8. Reitz, R. D., and Bracco, F. V., *Num. Fluid Mech.*, Vol. 5, 1982, p. 130.

9. Bowman, C. T., *Fossil Fuel Combustion (W. Bartock and A.F. Sarofim, Eds.)*, Wiley, 1991.

10. Kiehene, T. M., et. al., *Comb. Sci. Tech.*, V. 54, 1987, p. 1.

11. Freeman, G. and Lefebvre, A. H., *Comb. and Flame*, V. 58, 1984, p. 153.

12. Radhakrishnan, K., *Prog. in Astro. and Aero.*, V. 135, 1991, p. 83.

13. Radhakrishnan, K., *NASA-CR-179636*, 1987.

14. Miller, J. A., and Bowman, C. T., *Prog. in Energ. and Comb. Sci.*, V. 15, 1989, p. 287.

15. Anderson, D. A., *NASA-TM-X-71592*, 1975.

16. Amsden, A. A., et. al., *LA-11560-MS*, 1989.

Table I. Reduced Reaction Mechanism for Propane Combustion.

$H_2 + OH \rightleftharpoons H_2O + H$	$CO + OH \rightleftharpoons CO_2 + H$	$CH_2 + O_2 \rightleftharpoons CO_2 + 2H$
$O + OH \rightleftharpoons O_2 + H$	$CO_2 + O \rightleftharpoons CO + O_2$	$CH_2 + O_2 \rightleftharpoons CH_2O + O$
$O + H2 \rightleftharpoons OH + H$	$N_2 + O \rightleftharpoons N + NO$	$CH_2 + O \rightleftharpoons CO + H_2$
$H + O_2 \rightleftharpoons HO_2$	$N_2 + O_2 \rightleftharpoons 2NO$	$CH_2O \rightleftharpoons CO + H_2$
$H + HO_2 \rightleftharpoons H_2 + O_2$	$N + OH \rightleftharpoons NO + H$	$CH_2 + N_2 \rightleftharpoons HCN + NH$
$HO_2 + H \rightleftharpoons 2OH$	$C_3H_8 \rightarrow 3CH_2 + 2H$	$NH + H \rightleftharpoons N + H_2$
$HO_2 + OH \rightleftharpoons H_2O + O_2$	$C_3H_8 + O \rightarrow 3CH_2 + H_2O$	$HCN + O \rightleftharpoons CO + NH$

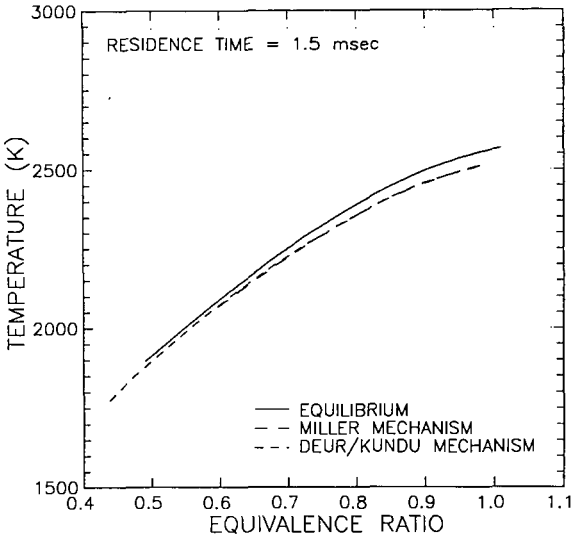

Figure 1. Equilibrium and Adiabatic Flame Temperature Comparison.

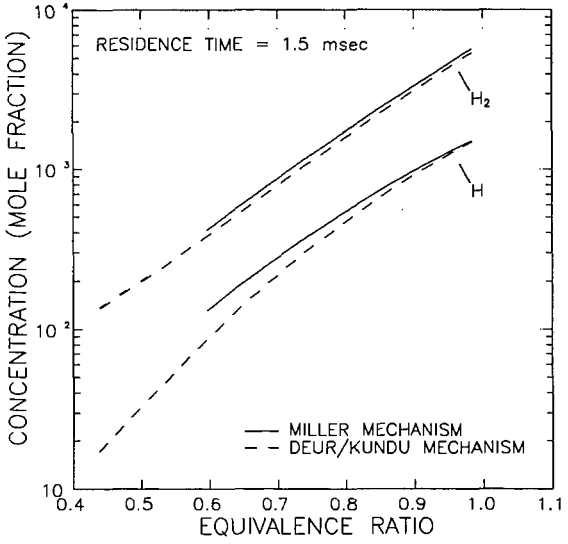

Figure 2. H and H_2 Species Concentration Comparison (Residence Time = 1.5 msec).

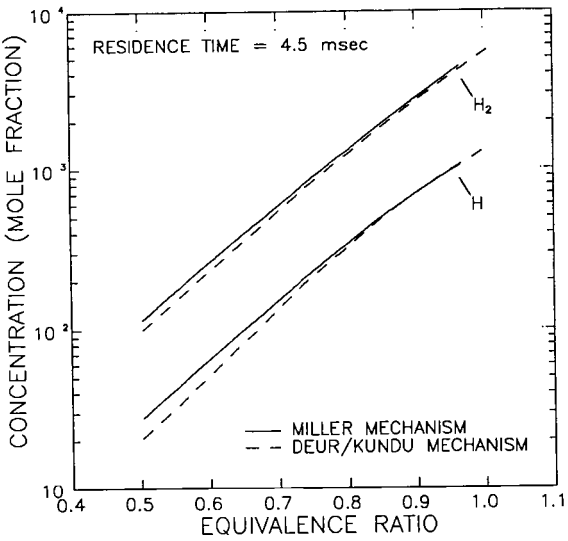

Figure 3. H and H_2 Species Concentration Comparison (Residence Time = 4.5 msec).

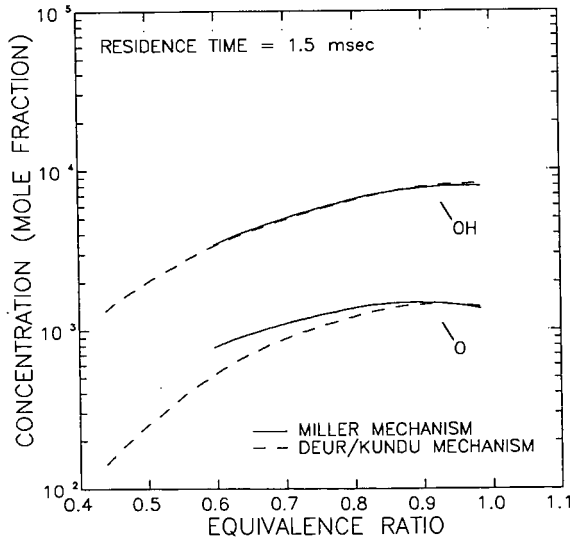

Figure 4. O and OH Species Concentration Comparison (Residence Time = 1.5 msec).

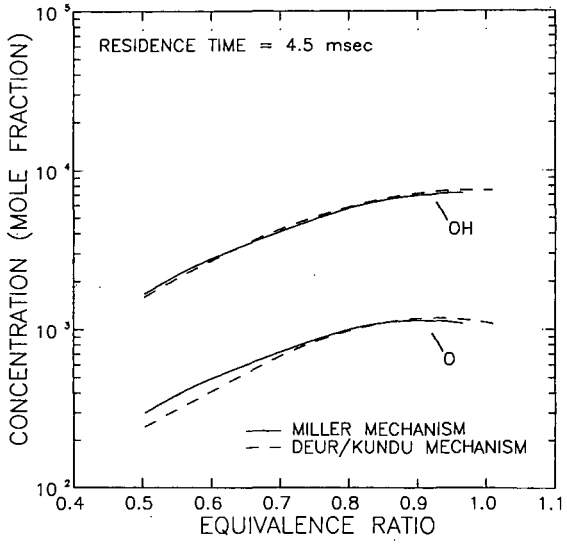

Figure 5. O and OH Species Concentration Comparison (Residence Time = 4.5 msec).

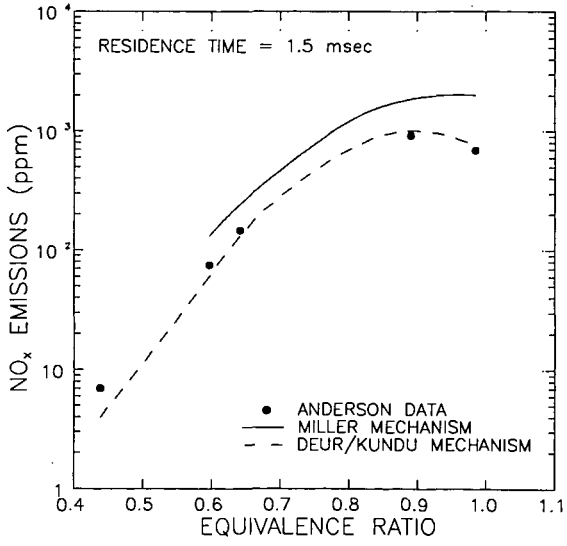

Figure 6. NO_x Emissions Comparison (Residence Time = 1.5 msec).

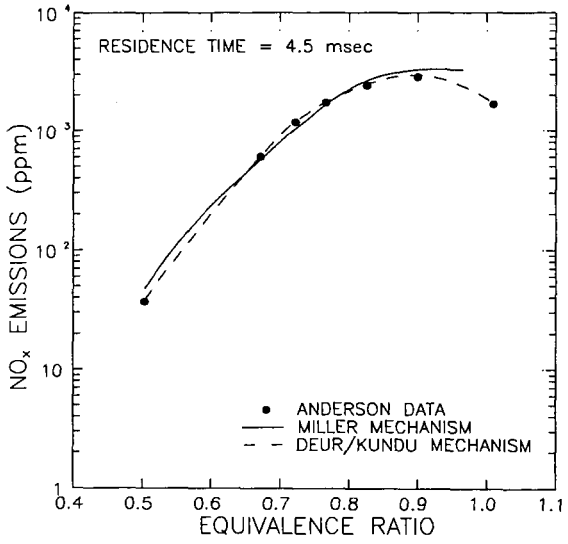

Figure 7. NO_x Emissions Comparison (Residence Time = 4.5 msec).

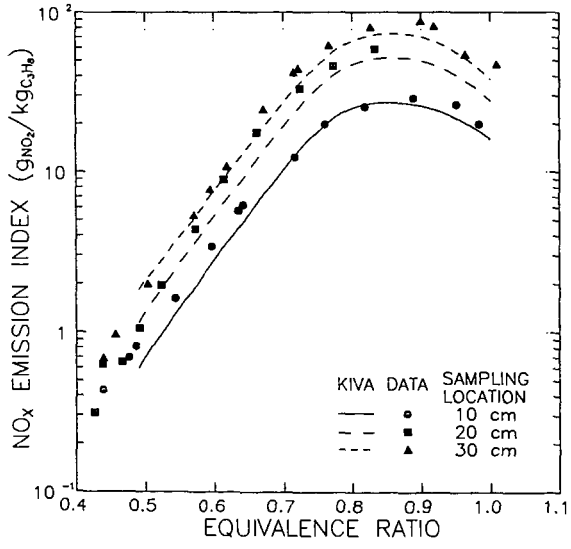

Figure 8. NO_x Emissions Comparison: Anderson Experimental Data vs. KIVA-II Predictions.